

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication No.: **0 167 872  
B1**

(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication:  
**28 March 1990**

(51) Int Cl.<sup>5</sup> **C 07 C209/16, C 07 C211/02,  
C07 C211/09, C 07 C213/02**

(21) Application number: **85107313.0**

(22) Date of filing: **13 June 1985**

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(54) **Method for the Production of Amines**

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(30) Priority: **19 June 1984 DE 3422610**

(43) Date of publication:  
**15 June 1986 Patent Bulletin 86/03**

(45) Announcement of patent granting:  
**28 March 1990 Patent Bulletin 90/13**

(84) Designated contracting states:  
**DE FR GB IT NL SE**

(56) Cited documents:  
**EP-A- 0 006 454  
EP-A- 0 009 590  
EP-A- 0 024 225  
EP-A- 0 127 874  
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(73) Patent Holder: **BASF Aktiengesellschaft  
Carl-Bosch-Strasse 38  
D-6700 Ludwigshafen (GERMANY)**

(72) Inventor: **Franzischke, Wolfgang, Dr. Ing.  
Franz-Lind-Strasse 1  
D-6713 Freinsheim (GERMANY)**  
Inventor: **Koernig, Wolfgang, Dr.-Chem.  
Dachsweg 5  
D-6901 Dossenheim (GERMANY)**  
Inventor: **Schroeder, Wolfgang, Dr.-Chem.  
Seebacher Strasse 51  
D-6702 Bad Duerkheim (GERMANY)**

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## Description

The present invention relates to a new method for the production of amines with one or two terminal dimethylamino groups by means of the reaction of optionally substituted alkanediols or N,N-dimethylaminoalkanols with dimethylamine in the gas phase at a pressure from 5 to 30 bar.

The conversion of diols with dialkylamines to the corresponding dialkylamino compounds is known. DE-A-2 824 908 describes a method for the production of bis(dialkylamino)alkanes, -oxa-alkanes and -aza-alkanes. The corresponding diols are made to react with a dialkylamine in the presence of catalysts containing copper and chromium at a temperature from 150 to 250°C in the liquid phase. Dialkylamine must then be used in a 2- to 10-fold stoichiometric excess. As follows from the examples, a high pressure must be applied (40 and 250 bar) to run the reaction. Finally, high residence times in the reactor are also required (2 to 4 hours) to achieve satisfactory yields.

According to the teachings of DE-A-3 104 738, alkanediols, ether diols, N,N-dimethylaminoalkanols or azaalkanols can be converted with dimethylamine in the gas phase on a copper catalyst to the corresponding permethylated amines, or optionally to their intermediates, the corresponding N,N-dimethylaminoalkanols.

To obtain satisfactory yields of the desired valuable products in this method, it is necessary to operate at atmospheric pressure. Even slight pressure increases, for example, to 3 bar, lead to an increased formation of byproducts.

In some cases, especially during the reaction of dimethylamine with diethylene glycol, N,N-dimethylaminoethanol or 1,4-butanediol, undefined high-boiling substances are formed, whose amounts can be up to 30%, in reference to the expected end products.

In addition to an undesired reduction in yield, the high-boiling substances also adversely affect the purity of the end products. Because of their thermal instability, they break down during distillation of the reactor output to cleavage products, and thus give rise to additional demanding purification operations during workup.

The object of the invention was to furnish a process that avoids the drawbacks of the prior art just outlined.

It was found that amines of general formula I



in which  $R^1$  denotes a hydroxyl group or dimethylamino group and A denotes an alkylene group with 2 to 6 carbon atoms, in which the carbon atom chain of the alkylene group can optionally be interrupted by oxygen atoms or  $N-R^2$  groups, in which  $R^2$  stands for a hydrogen atom or a lower alkyl group, are obtained by means of the reaction of alcohols with general formula II



in which  $R^1$  and A have the aforementioned meaning, with dimethylamine in the gas phase on a copper-containing catalyst, if the reaction is run at a temperature from 160 to 240°C and at a pressure from 5 to 30 bar and a molar ratio dimethylamine : mol equivalent of OH groups of 0.5:1 to 3:1 is maintained.

Appropriate alcohols that obey formula II include alkanediols with 2 to 6 carbon atoms, for example, 1,2-ethanediol, 1,4-butanediol, 1,5-pentanediol or 1,6-hexanediol, on the one hand.

On the other hand, oxaalkanediols or azaalkanediols are also suitable. In these compound classes the carbon atom chain of the mentioned alkanediols is interrupted by oxygen atoms or imino groups, in which the hydrogen atom of the imino groups can also be replaced by lower alkyl groups, like methyl, ethyl or propyl groups. For example, diethylene glycol, triethylene glycol or dipropylene glycol can be mentioned as oxaalkanediols, and diethanolamine, N-methyldiethanolamine, N-ethyldiethanolamine, dipropanolamine or N-methyldipropanolamine can be mentioned as azaalkanediols.

Finally, all N,N-dimethylaminoalkanols that are derived from the aforementioned diols by replacing an alcoholic hydroxyl group with an dimethylamino group are also suitable for the method according to the invention.

The products of the last-named class can be considered in the method according to the invention as both starting products and as intermediate or end products.

They are viewed as starting products, if they are to be converted to the corresponding bis(N,N-dimethylamino) compounds by means of the reaction with dimethylamine.

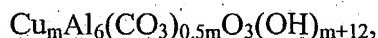
They are considered intermediates, if during reaction of the corresponding diols with methylamine, they form as mono(N,N-dimethylamino) compounds, intermediate to the bis(N,N-dimethylamino) compounds, and are converted to the corresponding bis compounds by means of the further reaction with dimethylamine.

Finally, they are treated as end products, if the reaction of the corresponding diols with dimethylamine is deliberately directed toward the class of N,N-dimethylaminoalkanols.

The employed catalysts are ordinarily supported catalysts and contain essentially just copper as the active component. The copper content in the catalyst is generally more than 20 wt.%, in reference to the catalyst. The copper can be applied to an inert support, for example,

by means of the impregnation with a copper salt solution, or also precipitated together with the inert material from a combined salt solution. Porous silica, alkaline earth silicate, aluminum oxide are suitable as inert material. Basic additives, like alkaline earth oxides, can also be contained in the catalyst.

A catalyst obtained by tempering of a carbonate containing basic copper and aluminum of the general composition



in which m denotes any value between 2 and 6, including fractional values, at a temperature from 350 to 700°C, is particularly preferred. The production of such basic carbonates containing basic copper and aluminum is described in DE-B-2 445 303.

The tempered compound can be converted to a particularly catalytically active form by means of the grinding and screening to an appropriate particle size distribution. However, by means of the known methods it can also be brought into the form of extrudates, pellets, spheres, rings, etc. Its activation occurs by means of a reduction, with the reduction expediently being conducted in a stage before the actual conversion. A hydrogen/nitrogen mixture containing 5 to 10 vol.% hydrogen is expediently used as the reducing gas. The reduction temperature is 140 to 200°C. The reduction preferably occurs at roughly atmospheric pressure.

It is essential for optimal running of the process according to the invention that a pressure from 5 to 30 bar, preferably 8 to 25 bar, be maintained.

The reaction partners must also be made to react in the gaseous state with complete mixing, in which the molar ratio of dimethylamine : mol equivalent OH groups must be 0.5:1 to 3:1, preferably 1:1 to 1.5:1. The value of 3:1 should not be surpassed, because the yield is substantially reduced by the formation of significant amounts of byproducts without raising the conversion of the reaction.

It is also essential to operate at a temperature of 160 to 240°C, preferably 180 to 220°C, and especially 200 to 220°C.

By maintaining the measures just outlined, the formation of the interfering high-boiling byproducts mentioned at the outset can be almost fully avoided. In addition, the formation of other known byproducts (for example, N-methylated cyclic imines) can be kept to a very low level by means of the method according to the invention. These results were surprising and not foreseeable. It is particularly surprising that the space-time yield is decidedly improved with increasing synthesis pressure.

The method according to the invention is advantageously run in a tubular reactor, in which the catalyst is generally situated within tubes that ordinarily have a diameter from 4 to 10 cm, preferably 4 to 6 cm.

It is recommended that the method according to the invention be run in the presence of a carrier gas. Hydrogen is preferably used as carrier gas. The gas mixture dimethylamine/hydrogen is subsequently referred to as "circulating gas"; it contains about 1 to 10 vol.%, especially 1 to 5 vol.%, dimethylamine.

The method according to the invention is expediently run by heating the alcohol components initially in a preheater and then mixing them with the circulating gas, which is also heated in a separate preheater. This mixture then enters an evaporator, where the alcohol component is fully evaporated. The resulting gas mixture is then brought to a temperature comparable to the reaction temperature required in the reactor. However, a somewhat higher temperature is expediently chosen in the evaporator, in order to compensate for possible heat losses on the way to the reactor.

The amounts of circulating gas and alcohol components are adjusted to each other, so that the partial pressure of the alcohol component at the temperature prevailing in the evaporator reaches about 30 to 80% of the saturation value. This guarantees that the alcohol component is fully evaporated and does not enter the reactor in the liquid state of aggregation.

The ratio of amount of gas to reactor volume is generally dimensioned so that the average residence time of the gas mixture in the reactor is less than 30 seconds. The gas volume  $V_G$  flowing through per unit time is understood to mean the volume calculated from the normal volume (for example, measured in  $\text{Nm}^3$ ) divided by the absolute pressure  $p$ . Reactor volume  $V_R$  is understood to mean the empty reactor space. The average residence time  $t$  therefore is:

$$t = \frac{p \cdot V_R}{V_G} < 30 \text{ seconds}$$

Allowing for the temperature expansion of the gas and space filling of the reactor space by the catalyst, the average residence time, however, is much smaller. It is generally less than 10 seconds.

This short residence time is sufficient to achieve good conversion during one pass through the reactor and to largely prevent the formation of byproducts at the same time.

The gas mixture leaving the reactor is condensed, during which the corresponding reaction products can be separated. The circulating gas then remains in the gaseous state of aggregation. Its dimethylamine content at this point is 1 to 5 vol.%. Since this concentration of

dimethylamine is relatively low, correspondingly little dimethylamine (about 5 wt.%) is also dissolved in the reaction condensate.

A small fraction (generally less than 5 vol.%) of the required amount of circulating gas is taken off as waste gas, in order to keep the percentage of gaseous byproducts low. The main amount is fed back to the preheater with a circulating gas pump. The hydrogen and dimethylamine losses are replenished on the way there, in order to close the gas loop.

The reaction products separated by condensation can be obtained in high purity by means of distillation at reduced pressure.

It should be noted that the distillates can contain incompletely methylated diamines, chiefly trimethylated diamines. Their total content in the pure distillate generally is below 1 wt.%. This fraction, however, is higher, the higher the dimethylamine excess during synthesis.

However, the mentioned trimethylated products cannot be separated by means of distillation. In the event that particularly pure end products are desired, these byproducts must still be eliminated. Adding a carboxylic acid anhydride to the dimethylamine-free crude product, for example, acetic anhydride or phthalic anhydride, in an amount of 1 mol acid anhydride per mol of trimethyldiaminoalkane has been shown to work. The contamination is thus converted to a high-boiling substance that no longer interferes during the distillation of the end product.

As already mentioned, the formation of the corresponding bis(N,N-dimethylamino) compounds is particularly favorable, if the participating N,N-dimethylaminoalkanol is used as the reaction partner. In some cases, this product can also be advantageously obtained by means of an independent reaction. (N,N-dimethylaminoethanol, for example, is easy to produce by means of the reaction of ethylene oxide with dimethylamine). In other cases, this compound class is not readily available. However, it forms during the reaction of the corresponding diol with dimethylamine, in each case, as an intermediate.

By setting suitable reaction conditions, a situation can be achieved in which (N,N-dimethylaminoalkanol) predominates as the reaction product. This is achieved, for example, by reducing the reaction temperature, by shortening the residence time, a smaller feed of dimethylamine or by combining these measures.

The bis(N,N-dimethylamino) compounds can be used, for example, as a catalysts in polyurethane production.

The mono(N,N-dimethylamino) compounds are valuable intermediates in dye production. However, they can also be mixed with a corresponding amount of the corresponding diol and fed back to the reaction loop.

The following examples will further explain the invention.

**Example 1**

1,2-bis(dimethylamino)ethane

N,N-dimethylaminoethanol served as the starting product for this synthesis:

The reaction was run in a tubular reactor with an inside diameter of 4 cm and a total length of 200 cm. The catalyst packing was situated within the tube between two layers of metal Raschig rings. It consisted of 2 L of a copper catalyst (unreduced form) and was prepared according to DE-B-2 445 303. The reactor was enclosed with a jacket tube, through which the correspondingly heated heat transfer oil was passed.

The catalyst was initially reduced at a temperature of 140 to 200°C with a hydrogen/nitrogen mixture flowing through the reactor, containing 5 to 10 vol.% hydrogen.

After reduction was complete, the following reaction conditions were set:

Total pressure:	9 bar
Reaction temperature:	190°C
Circulating gas amount:	130 L (under pressure) per liter of catalyst and hour
Circulating gas composition before the reactor:	6 vol.% dimethylamine 94 vol.% hydrogen

0.12 L/L of catalyst per hour and N,N-dimethylaminoethanol were then pumped through the preheater that had been heated to 190°C and mixed with the circulating gas. This mixture was fed to the evaporator, in which the N,N-dimethylaminoethanol was fully evaporated. The gas mixture leaving the evaporator had a temperature of 200°C and was now passed through the reactor, where conversion occurred under almost isothermal reaction conditions.

The conversion of N,N-dimethylaminoethanol per pass was 55%; the yield of 1,2-bis-(N,N-dimethylaminoethanol) was 94%.

**Example 2 (Comparison)**

The reaction was run similarly to example 1, but at atmospheric pressure. The conversion was 50%; the yield of 1,2-bis(N,N-dimethylaminoethanol), however, was only 60%.

**Example 3**

Bis(dimethylamino)diethyl ether and N,N-diethylaminodiglycol

The arrangement of example 1 was used and operated as follows:

Total pressure:	7 bar
Reaction temperature:	205°C
Amount of circulating gas:	360 L (under pressure)/L of catalyst and hour
Dimethylamine content in circulating gas:	
before the reactor:	5 to 7 vol. %
after the reactor:	2 to 3 vol. %
Diglycol feed:	0.3 L/L of catalyst and hour

The concentrate contained (without dimethylamine and reaction water) 85 wt.% of bis(N,N-dimethylamino)diethyl ether, 55 wt.% of N,N-dimethylaminodiglycol, 1 wt.% of unconverted diglycol and a total of 9 wt.% of several unidentified byproducts. By means of a simple distillation at reduced pressure (50 mbar), both reaction products were recovered in good purity (in each case, more than 98%).

Diglycol conversion was 99%, the total yield about 90%.

**Example 4 (Comparison)**

The reaction was run similarly to example 3, but at atmospheric pressure. The diglycol feed was 0.08 L per L of catalyst and hour. A diglycol conversion of 85% was obtained with a total yield of 70%.

If the glycol feed was increased toward the value of example 3, both the conversion and total yield dropped further.



## Example 5

N,N,N',N'-tetramethyldiaminohexane

The arrangement of example 1 was used and operated as follows:

Total pressure:	8 bar
Reaction temperature:	210°C
Amount of circulating gas:	500 L (under pressure)/L of catalyst and hour
Dimethylamine content in circulating gas:	
before the reactor:	5 to 7 vol.%
after the reactor:	2 to 3 vol.%
Feed to the evaporator:	Hexanediol solution in methanol with 70 wt.% diol 0.4 L solution/L of catalyst and hour

Fractional distillation and gas chromatographic analyses yielded the following values for the composition of the condensate:

Reaction water	11 wt.%
Methanol	18 wt.%
Dissolved dimethylamine	8 wt.%
N-methylhexamethyleneimine	4 wt.%
Tetramethyldiaminohexane	53 wt.%
Dimethylaminohexanol	1 wt.%
Hexanediol	0.5 wt.%
Other	4 wt.%
Distillation residue	0.5 wt.%

The desired product was obtained in good purity (above 98%) by simple distillation at reduced pressure.

**Example 6 (Comparison)**

If the reaction is run at atmospheric pressure, a result similar to that of example 5 is obtained under the following conditions:

Reaction temperature:	180°C
Dimethylamine content in circulating gas:	
before the reactor:	10 to 15 vol. %
after the reactor:	5 to 10 vol. %
Feed to the evaporator:	0.1 L solution/L of catalyst and hour

The condensate had a composition similar to that of example 5, the only difference being that it contained up to 5 wt. % of unidentified high-boiling fractions (distillation residue).

If the feed amount is raised above the stated amount of 0.1 L/L•h, the percentage of dimethylaminohexanol and hexanediol in the condensate increases. If the temperature is also increased, the percentage of N-methylhexamethyleneimine and the high-boiling fraction in the condensate is also increased, whereas the percentages of dimethylaminohexanol and hexanediol simultaneously decline.

This "trend analysis" demonstrates that the operating conditions for example 6 lie close to a relative optimum, so that changes cause a deterioration in the result, as long as the synthesis pressure is left constant at atmospheric pressure.

Example 6 also shows an advantage of increased pressure: the throughput can be increased with the same synthesis result as at atmospheric pressure.

**Example 7**

N,N,N',N'-tetramethyldiaminohexane

The procedure of example 5 was followed, the only difference being that a methanol-free hexanediol melt is used as the feed to the evaporator in an amount of 0.2 L per L of catalyst and hour.

Fractional distillation and gas chromatographic analyses yielded the following values for the composition of the condensate:

Reaction water	15 wt. %
Dissolved dimethylamine	5 wt. %
N-methylhexamethyleneimine	5 wt. %
Tetramethyldiaminohexane	68 wt. %
Dimethylaminohexanol	1 wt. %
Hexanediol	-
Other	6 wt. %
Distillation residue	-

### Example 8 (Comparison)

The procedure of example 6 was followed, the only difference being that a methanol-free hexanediol melt was used as feed to the evaporator in an amount of 0.1 L per L of catalyst and hour.

Fractional distillation and gas chromatographic analyses yielded the following values for the composition of the condensate after 48 hours of operation:

Reaction water	13 wt. %
Dissolved dimethylamine	8 wt. %
N-methylhexamethyleneimine	4 wt. %
Tetramethyldiaminohexane	47 wt. %
Dimethylaminohexanol	14 wt. %
Hexanediol	1 wt. %
Other	5 wt. %
Distillation residue	8 wt. %

With continuing experiment time, the condensate continuously changed, until the percentage of dimethylaminohexanol became greater than the percentage of the desired tetramethyldiaminohexane.

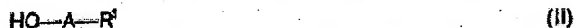
This example 8 clarifies another advantage of increased pressure: the addition of methanol, which is expedient at atmospheric synthesis pressure, is not necessary at an elevated pressure.

## Claims

1. A process for preparing an amine of the general formula I



where  $\text{R}^1$  is hydroxyl or dimethylamino and A is alkylene of from 2 to 6 carbon atoms which may be interrupted by oxygen or  $-\text{NR}^2$ , where  $\text{R}^2$  is hydrogen or lower alkyl, by reacting an alcohol of the general formula II



where  $\text{R}^1$  and A are each as defined above, with dimethylamine in the gaseous phase over a copper-containing catalyst, which comprises performing the reaction at from 160 to 240 °C and from 5 to 30 bar while maintaining a molar ratio of dimethylamine : mole equivalent of OH groups of from 0.5 : 1 to 3 : 1.

2. A process as claimed in claim 1, wherein a molar ratio of dimethylamine : mole equivalent of OH groups of from 1 : 1 to 1.5 : 1 is maintained.

3. A process as claimed in claim 1, wherein the reaction is carried out at from 8 to 25 bar.

4. A process as claimed in claim 1, wherein the copper-containing catalyst used is obtainable by heating a basic copper/aluminum carbonate of the general composition



where m is any desired integer or non-integer from 2 to 6, at from 350 to 700 °C.